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THE DRIVING ENERGY OF PHYSICO-CHEMICAL REACTION, AND ITS TEMPERATURE COEFFICIENT.

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Every beginner in Physical Chemistry of course notices the similarity in form of the equations of Clausius and van't Hoff, $\frac{d \ln P}{d T} = \frac{\lambda}{R T^2}$ and $\frac{d \ln K}{d T} = \frac{U}{R T^2}$. The differences in the interpretation of the symbols are the only hindrance to the welding of the two equations into one. P usually consists of a single quantity, a pressure, while K is usually a product of concentrations. On the other hand, the second member of the equation sometimes includes work ($\lambda = A - U$) and sometimes contains simply the diminution of the internal energy (U) of a process conducted at constant volume.

Since these distinctions are so confusing that errors from the lack of proper discrimination have crept into some of our best and most helpful treatises, the present paper, which is a treatment of the subject from a single point of view, may be of assistance to students who have not mastered the matter. I have found it advantageous, both in teaching and in thinking, to look at the whole field from the point of view of *pressure*. This practice has recently received support in an interesting article by Arrhenius * on the speed of reactions.

That the pressures affecting a given reaction should exert the deciding influence in determining the magnitude and direction of a chemical change, is no more astounding than that the resultant of mechanical forces should be the agent determining the change of position of finite masses. Hence the consideration of pressure, which has the dimensions of an intensity, seems to be a more direct method of studying the progress of a reaction

* Zeitschr. phys. Chem. **28**, 317 (1899).

than does the consideration of volume or entropy, which have the dimensions of capacities merely.

There are of course many possible ways of attacking the subject mathematically. Perhaps the simplest is given below.

In his recent comprehensive and exceedingly interesting paper on equilibrium and free energy,* Gilbert N. Lewis has shown that the following equation is a very general one, applying to both homogeneous and heterogeneous systems, but rigorously accurate only when the system is composed of ideal gases, ideal solutions, and "condensed phases" of constant volume. This is of course the equation of van't Hoff.

$$\frac{d \ln \frac{v_2^{n_2} v'_2{}^{n'_2} \dots}{v_1^{n_1} v'_1{}^{n'_1} \dots}}{dT} = \frac{d \ln \frac{c_1^{n_1} c'_1{}^{n'_1} \dots}{c_2^{n_2} c'_2{}^{n'_2} \dots}}{dT} = + \frac{U}{RT^2}. \qquad (1)$$

In this expression v means molecular volume; T, absolute temperature; c, concentration $\left(= \frac{1}{v}\right)$; n, the number of reacting molecules of any given molecular species; U, the diminution in the internal energy of the process, or the heat of reaction at constant volume; and R, the gas constant (1.98 calorie-units, or better 8.31 c. g. s.). The products of a reaction are indicated by a subscript 2, the factors by 1. The chief disadvantage of the equation for practical purposes is the fact that the numerator of the second member does not always represent the actual heat of the reaction, since it does not take account of the work which the reaction may involve on account of changing volume.

Let us now introduce pressure instead of concentration into this expression. $c = \frac{p}{RT}$, hence the expression becomes

$$\frac{d}{dT} \ln \frac{(RT)^{(n_2 + n'_2 \dots)} p_1^{n_1} p'_1{}^{n'_1} \dots}{(RT)^{(n_1 + n'_1 \dots)} p_2^{n_2} p'_2{}^{n'_2} \dots} = \frac{U}{RT^2}.$$

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* These Proceedings, **35**, 1 (1899); Z. phys. Chem. **32**, 364 (1900).

I am much indebted to Dr. Lewis for valuable mathematical criticism of the present paper. To Dr. Edgar Buckingham also I owe thanks for his interest, and for valuable suggestions as to matters of detail. Since reading the manuscript the latter has derived the "reaction-isobar" according to the method of Duhem; but in the present exposition I have retained the original derivation, because it is much simpler than his more rigorously exact method, as well as because most readers of physical chemistry are accustomed to the method and nomenclature of Nernst.

Cancelling the unnecessary powers of RT, we have

$$\frac{d}{dT}\ln\frac{(RT)^{(n_2+n'_2\ldots-n_1-n_1)}p_1^{n_1}p'_1{}^{n'_1}\ldots}{p_2^{n_2}p'_2{}^{n'_2}\ldots}=\frac{U}{RT^2}. \qquad (2)$$

Let us consider for the sake of argument a case in which

$$(n_2+n'_2\ldots-n_1-n'_1)=N$$

is positive, that is, a case in which the total number of gram-molecules in the product is greater than that in the reacting mixture before the reaction took place. The expression then becomes

$$\frac{d}{dT}\ln\frac{(RT)^N p_1^{n_1}p'_1{}^{n'_1}\ldots}{p_2^{n_2}p'_2{}^{n'_2}\ldots}=\frac{U}{RT^2}. \qquad (3)$$

From this pressure-equation at constant volume we may omit $d\ln R$, because R is a constant. Thus

$$\frac{d\ln\dfrac{p_1^{n_1}p'_1{}^{n'_1}\ldots T^N}{p_2^{n_2}p'_2{}^{n'_2}\ldots}}{dT}=\frac{U}{RT^2}. \qquad (4)$$

Here two cases may arise. If $N=0$, that is, if the osmotic or gas pressure (or total number of molecules) does not change during the reaction, the pressure remains constant. Mathematically, T^N becomes 1 and hence disappears. On the other hand, if $N\gtrless 0$, T^N becomes a serious factor in the equation, affecting immensely the temperature coefficient of the "mass-law constant."

The numerator of the second term of this modified equation of van't Hoff still consists merely of U; hence if the equation is to be used with data obtained under constant pressure, the observed heat of reaction must be corrected for the work done during expansion. For this reason its prototype has been called the "reaction isochor" by Nernst; it represents immediately the observed conditions only when the reaction takes place in constant volume. The introduction of the correction causes an interesting simplification.

At constant pressure the heat evolved during the reaction would be less than U, because the work NRT is done against constant pressure; hence we shall be obliged to subtract $\dfrac{NRT}{RT^2}=\dfrac{N}{T}$ from each side of the equation in order that the numerator of the second member may truly indicate the actual conditions. But

$$\frac{N}{T} = \frac{N d \ln T}{d T},$$

hence by simply subtracting the equations we obtain

$$\frac{d}{d T}\left(\ln \frac{p_1^{n_1} p'_1{}^{n'_1} \ldots}{p_2^{n_2} p'_2{}^{n'_2} \ldots} + N \ln T\right) - \frac{N d \ln T}{d T} = \frac{U}{R T^2} - \frac{N R T}{R T^2}.$$

Simplifying, and noting that $-U + NRT = \lambda$, the heat actually absorbed in the reaction, we may write

$$\frac{d}{d T} \ln \frac{p_1^{n_1} p'_1{}^{n'_1} \ldots}{p_2^{n_2} p'_2{}^{n'_2} \ldots} = \frac{-\lambda}{R T^2}. \tag{5}$$

Here $-\lambda$ signifies heat *given out* when the reaction takes place under constant gas or osmotic pressure, because λ signifies heat absorbed, or latent heat. The equation states that when pressures are being compared, the latent heat under constant pressure is the term to be used in calculation.

Hence at constant outside pressure the heat observed in any reaction bears a very simple relation to the acting pressures which take part in that reaction, just as at constant volume the concentrations are similarly related to the observed evolution of heat. This equation may be called the "Reaction-isobar," on account of the fact that constancy of total pressure is the condition essential to its immediate application. The equation of Clausius is a special case of this law.

Evidently these reactions isobar and isochor may now be combined into one, for the obstacles to this union are now removed. Before combining them, it is advantageous to examine into the meaning of

$$d \ln (RT)^N = d \ln T^N,$$

which constitutes the only puzzling difference between them.

The physical meaning of this important factor in the equation is interesting. From its mode of introduction into equation (2), this term is clearly the representative of the pressure caused by an addition to the total number of molecules in a given space. When the total pressure is artificially maintained at a constant value, $\ln T^N$ disappears from the equation, just as it does when the pressure remains constant because the total number of molecules present is not increased by the reaction. This is equivalent to defining N in its present situation as a direct function of the *increase in the total pressure of the reacting substances* during the reaction. In order to avoid conflict with the original definition of N, we

shall call this newly defined exponent N'. Mathematically, the inspection of the equations (4) and (5) shows that the expression

$$N' = \mathfrak{N}\frac{P_2 - P_1}{P_1}$$

(where $\mathfrak{N}$ is the total number of gram-molecules in the initial reacting mixture, and P_1 and P_2 the initial and final total pressures respectively) is true either for constant pressure or constant volume. Whether this still holds true for the ill-defined cases where neither volume nor pressure is constant, we shall not at present determine. In constant volume, according to this definition, $N' = N$; under constant pressure, likewise according to this definition, $N' = 0$. With the help of this new definition, together with the use of the symbol Q to signify in general the actually observed latent heat of the reaction, it becomes possible to combine the reactions-isochor and isobar into one equation, from which either may be logically obtained again, according to the circumstances attending the reaction. Thus, we may write: —

$$\frac{d}{dT}\ln\frac{p_1^{n_1}p'_1{}^{n'_1}\ldots T^{N'}}{p_2^{n_2}p'_2{}^{n'_2}\ldots} = -\frac{Q}{RT^2}, \qquad (6)$$

which is a general expression for the temperature coefficient of the equilibrium ratio * of dilute reactions.

If the total osmotic or gas pressure is kept constant, $N' = 0$, hence $T^{N'} = 1$, and disappears, and $Q = \lambda = NRT - U$. This is the reaction isobar. If, on the other hand, the volume is kept constant, $T^{N'}$ represents the increase in pressure which at constant pressure would have represented work, and $-Q = U$. This is the reaction isochor. If N' is 0, and $-Q = U$, the equation is both isochor and isobar.

For the general expression (6) which defines the temperature-coefficient of the equilibrium ratio I propose the name "reaction metatherm" (*μετά, between*). The chief advantage which it possesses over the concentration equation is the fact that its term $-Q$ is always the heat actually evolved, whether work is done or not, as well as the fact that it deals with the more rational dimension, — pressure.

Since Q is the heat really observed, it is clear that the expression must be the analytical statement of the theorem of Maupertuis or Le

* This satisfactory name is due to Lewis. "Mass law constant" is less satisfactory, because the quantity is not constant, and the law seems to be due to pressure rather than to mass.

Chatelier as far as heat is concerned. In order to trace this evident necessity, one must assume a somewhat puzzling inverted attitude. The pressures indicated by the formula define a condition of equilibrium, not a condition of action. It is clear, then, that a small pressure in the numerator of the logarithmic expression means a great tendency towards the denominator. That is, a growing denominator means an increasing tendency to change from factors to products. But the logarithms in the denominator take the minus sign, or the sign of Q, which represents heat absorbed. Hence a reaction which absorbs heat evidently must be pushed farther by increasing temperature.

The inverted attitude just mentioned may be easily remedied by considering carefully the nature of the quantities involved. We have seen that the expression

$$\ln \frac{p_1^{n_1} p'_1{}^{n'_1} \dots}{p_2^{n_2} p'_2{}^{n'_2} \dots} = k,$$

the familiar "mass-law" expression for equilibrium expressed in terms of pressure, seems to represent the resultant reacting tendency of a given reaction at constant temperature; because it is this quantity which is concerned with the theorem of Maupertuis. When concentrations are used, it is difficult to imagine any physical meaning in this equilibrium ratio; but when the expression is conceived of in terms of pressure, we may look upon k as an opposing tendency which has been balanced by the ratio of the pressures observed. That is, we may call k the "reaction tendency." This means not merely pressure, but work; because the expression $RT\int\frac{dp}{p}$ from which it was originally derived means work. It represents then the *variable* factors in the "driving energy" of the reaction.

We may conceive of this reaction tendency as consisting of a number of individual reacting tendencies, one for each substance. But the pressures in the pressure-equilibrium ratio do not directly represent the individual reacting tendencies of the substances represented. They are only the pressures which remain in equilibrium when all the reacting forces have been balanced. When under the circumstances a given individual pressure is small, we must ascribe to that substance a great reacting tendency, and *vice versa*. Thus it seems to me probable that each of these pressures must have a term in the function k which corresponds to its tendency to react, and this individual tendency we shall call $\ln z$, — a term which will be in the numerator when the correspond-

ing pressure is in the denominator, and *vice versa*. The reasoning may be stated in the form of an equation: —

$$\ln \frac{p_1^{n_1} p'_1{}^{n'_1} \dots}{p_2^{n_2} p'_2{}^{n'_2} \dots} = \ln \frac{z_2^{n_2} z'_2{}^{n'_2} \dots}{z_1^{n_1} z'_1{}^{n'_1} \dots}.$$

This equation is simply a definition of the values z, which are made logarithmic from analogy to the other pressures. One must bear in mind, however, that this z, or "physico-chemical potential," need not be the *reciprocal* of p; for the condition of equilibrium demands only that the *total sum of the logarithms* on each side must be equal, and not that the individual opposites are immediate functions of one another. The p values depend of course upon the amount of substance present; while the z values are constant for any given temperature, because they are by definition the constant factors of a constant. Any constant tendencies, not given by the differential equation, may hence be included among the z values.

Transposing the second member, we obtain

$$\ln \frac{p_1^{n_1} p'_1{}^{n'_1} \dots z_1^{n_1} z'_1{}^{n'_1} \dots}{p_2^{n_2} p'_2{}^{n'_2} \dots z_2^{n_2} z'_2{}^{n'_2} \dots} = 0. \qquad (7)$$

This expression may be written

$$n_1 \ln (p_1 z_1) + n'_1 \ln (p'_1 z'_1) - n_2 \ln (p_2 z_2) - n'_2 \ln (p'_2 z'_2) \dots = 0.$$

Except for its logarithmic form and the substitution of pressure for mass, this equation reminds one of Berthollet's old statement concerning chemical action. It is a fundamental equation of chemical equilibrium in dilute or ideal mixtures.

Stated in words, the equation reads: Each molecule taking part in a reaction may be said to possess at any given temperature a reacting tendency which is the logarithm of the product of its constant physico-chemical potential and variable observed pressure. Obviously the logarithmic arrangement is so convenient as almost to demand its adoption, although the same idea might have been expressed otherwise. One may say, for example, that in equilibrium the algebraic sum of the opposing energies concerned is zero, — almost an axiom. The logarithmic equation is a plausible hypothesis which is concordant with the well known Nernst equation, and with many other natural tendencies.

The substitution of the new value for k instead of its pressure equivalent in the equation gives us a less inverted view of the theorem of Maupertuis: —

$$\frac{d \ln \frac{z_2^{n_2} z'_2{}^{n'_2} \ldots T^{N'}}{z_1^{n_1} z'_1{}^{n'_1} \ldots}}{dT} = \frac{-Q}{RT^2}.$$

It will be seen at once that the sum of the reacting tendencies of the initial substances $\ln z_1^{n_1}$, $\ln z'_1{}^{n'_1}$, etc., agree in sign with Q; that is, a reaction which absorbs heat will have a greater tendency to take place as the temperature rises.

Besides comprehending the partial pressures within a single phase, and the "physico-chemical potentials" of the various substances which are in it, the pressure equations may be applied to the relations between two phases; since the equation from which they were derived is true for ideal heterogeneous equilibrium. We may then introduce into the equation phase-pressures, such as vapor or solution tensions, which are exerted in opposition to gas or osmotic pressures respectively. Such phase-pressures will be represented, for the sake of convenience, by the usual designation P.

A few simple physical examples may now be cited, to show that the point of view is not inconsistent with the facts in these cases. For example, in the case of an evaporating liquid, we may say that the force concerned is the vapor tension, which therefore takes the place of z_1. It is placed in the denominator because the process absorbs heat. There are no opposing forces except the constant gas pressure against which the evaporation proceeds; hence the equilibrium equation becomes

$$\ln \frac{k}{P} = 0,$$

— an obvious truth; and the reaction-metatherm reduces at once to the equation of Clausius.

A more complicated case is the evaporation of water from a crystallized salt; but the treatment is equally simple. The water has a certain reacting tendency or driving energy which manifests itself as a definite pressure at each temperature. Precisely the same explanation applies to calcic carbonate, or any other similar case. The simplicity of the conception of this reacting tendency seems to commend itself as an improvement over the usual involved treatment, since it does not demand that all the solid should be vaporized in order to effect the change.

A still more complicated case is the evaporation of ammonic sulphydrate. Here we have to consider the physical tendency of the evaporating substance, which is balanced by the pressure of the ammonic sulphy-

drate, as well as the physico-chemical potentials and actual pressures of the three molecular species. The equation of equilibrium would then be

$$\ln k \frac{p_1 (p_2 z_2)^{NH_3} (p'_2 z'_2)^{H_2S}}{P (p_1 z_1)^{NH_4SH}} = 0.$$

This expression is an analysis of the forces which are at work in maintaining equilibrium. p_1, the pressure of the undissociated NH_4SH, occurs first in the numerator as opposing P, the sublimation tension of the solid substance, and then in the denominator as a factor of the chemical reacting tendency of the ammonic sulphydrate. These two of course cancel, and since at constant temperature P and all the z values are constant, we obtain for the chemical part of the equilibrium the familiar expression

$$p_2 p'_2 = k'.$$

This is entirely in accord with the results of Isambert, and is undoubtedly true.

Many other examples of the application of the pressure equations might be given. For example, the dissociation of nitric peroxide is easily treated by the reaction-isobar, while that of hydriodic acid needs merely the simplest form of all, which is both isochor and isobar. Moreover, it is obvious that upon introducing electrolytic solution tensions and osmotic pressures into the reaction isobar, it becomes at once the well known expression for the temperature coefficient of electromotive force. In short, whenever pressures are under consideration, one of the two special forms of the equations above affords a ready means of treatment.

The results of this paper may be summarized as follows: —

1. It is pointed out that the study of pressure affords a more direct method of analyzing the progress of a reaction than the study of volume, concentration, or entropy.

2. An expression called the "reaction-metatherm" has been evolved which represents in terms of pressure the temperature coefficient of the equilibrium ratio of ideal physico-chemical reaction.

3. Since this equation always contains in its second member the heat actually evolved in the reaction, whether under constant volume or constant pressure, it is a mathematical expression of the Theorem of Maupertuis or Le Chatelier.

4. Moreover, since the equation represents this fundamental theorem, its logarithmic quantity must represent the variables in the reacting tendency, or the driving energy of reaction.

5. When analyzed, this equation shows that the part played by each substance in a reaction may be considered as the logarithm of the product of its "physico-chemical potential" and its actually present pressure.

6. The reaction metatherm may be simplified into a reaction-isobar and a reaction-isochor, according as the pressure or volume is kept constant during the reaction.

7. While the reaction-isobar, expressed in terms of pressure, offers the most convenient basis for the calculation of the cases to which it is applicable, results obtained under constant volume are more conveniently calculated if the reacting substances are expressed in terms of concentration, according to the equation of van't Hoff.

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